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The pentacoordinated $[Cr(CO)_5]^{2-}$ dianion in $[2,2,2\text{-crypt-K}]_2[Cr(CO)_5]$ ethylenediamine monosolvate

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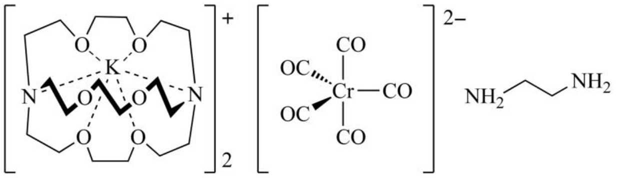
Bis[(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)potassium(+)] pentacarbonylchromate(2−) ethylenediamine monosolvate, $[K(C_{18}H_{36}N_2O_6)]_2[Cr(CO)_5]\cdot C_2H_8N_2$, was obtained from the reaction between $K_3Cd_2Sb_2$ and $Cr(CO)_6$ in ethylenediamine in the presence of the macrocyclic 2,2,2-crypt ligand. The structure provides the first crystallographic characterization of the pentacoordinated $[Cr(CO)_5]^{2-}$ dianion. The central Cr^{III} atom is coordinated by five carbonyl ligands in a distorted trigonal–bipyramidal geometry. The distribution of the Cr—C bond lengths indicates a greater degree of back bonding from Cr^{III} to the equatorial carbonyl ligands compared with the axial carbonyl ligands.

Comment

The chromium–carbonyl dianions $[Cr(CO)_5]^{2-}$ and $[Cr_2(CO)_{10}]^{2-}$ are used extensively for the preparation of substituted chromium–carbonyl complexes. $[Cr_2(CO)_{10}]^{2-}$ has been synthesized by various methods, such as reduction of $Cr(CO)_6$ using C_8K in dry deoxygenated tetrahydrofuran (THF) (Ungurenasu & Palie, 1975), KSi in DME/toluene (DME is 1,2-dimethoxyethane; Hey-Hawkins & von Schnering, 1991), Na_2Tl in THF/DMF (DMF is dimethylformamide; Borrmann *et al.*, 1997*a*) and $[Pb_2Ch_3]^{2-}$ (Ch is Se or Te) in THF/ethylenediamine (Borrmann *et al.*, 1997*b*). Preparation of $Na_2[Cr(CO)_5]$ has been achieved by the reduction of $[Cr(CO)_5NMe_3]$ using alkali metal (Li^+ or Na^+) naphthalenide in dry THF (Maher *et al.*, 1985, 1986). An increased stirring time for this reaction (>12 h) and metathesis with (PPN)Cl (PPN is $Ph_3P{=}N{=}PPh_3^+$) produces $(PPN)_2[Cr_2(CO)_{10}]$ (Lee *et al.*, 1996). Related compounds containing a six-coordinated Cr atom have also been reported, for example, $(PPh_4)[HCr(CO)_5]$ (Darensbourg *et al.*, 1982) and $[(NHMe_2)Cr(CO)_5]$ (Rogers & Alt, 1992). To date, however, there have not been any crystal structures reported containing the five-coordinated $[Cr(CO)_5]^{2-}$ dianion. In this work, we have explored the reactions between heteropolyatomic Zintl anions and $Cr(CO)_6$ by sequestering K^+ cations with the macrocyclic ligand 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane). Supported by ethylenediamine as the reaction solvent, this provides a strongly reducing environment, and the title compound, (I), was obtained as single crystals. The mechanism for the formation of $[Cr(CO)_5]^{2-}$ *via* reductive elimination (Maher *et al.*, 1985) is shown in the reaction scheme below.

$$Cr(CO)_6 \xrightarrow{e^-} [Cr(CO)_6]^{\cdot-} \xrightarrow{-CO} [Cr(CO)_5]^{\cdot-} \xrightarrow{e^-} [Cr(CO)_5]^{2-}$$



(I)

Compound (I) contains two crystallographically independent $[2,2,2\text{-crypt-K}]^+$ cations (Fig. 1), a $[Cr(CO)_5]^{2-}$ dianion (Fig. 2) and an ethylenediamine solvent molecule. Although the compound crystallizes in the space group *P*1, the $[2,2,2\text{-crypt-K}]^+$ cations are related by pseudo-inversion symmetry: overlay of one independent cation with an inversion-generated copy of the other gives an r.m.s. deviation of 0.06 Å. The structure is similar to that of $[2,2,2\text{-crypt-K}]_2[Cr_2(CO)_{10}]$ [Borrmann *et al.*, 1997*b*; Cambridge Structural Database (Allen, 2002) refcode RERYUI]. In (I), the $[2,2,2\text{-crypt-K}]^+$ cations form layers in the (100) plane, with a hexagonal arrangment of cations related by pseudo-inversion centres (Fig. 3). The $[Cr(CO)_5]^{2-}$ dianions and ethylenediamine solvent molecules occupy voids within the hexagonal arrangement and between the layers. Essentially identical layers of $[2,2,2\text{-crypt-K}]^+$ cations are present in the (100) plane of $[2,2,2\text{-crypt-K}]_2[Cr_2(CO)_{10}]$, and $[Cr_2(CO)_{10}]^{2-}$ dianions occupy similar sites in the voids within and between these layers (Fig. 4). In this case, however, the $[Cr_2(CO)_{10}]^{2-}$ dianions are situated on centres of inversion in the space group $P\bar{1}$.

The principal point of interest in (I) is the structure of the pentacoordinated $[Cr(CO)_5]^{2-}$ dianion. As shown in Fig. 2, the central Cr^{III} atom is coordinated by five carbonyl ligands in a trigonal–bipyramid geometry, with atoms C1 and C3 in the axial sites and atoms C2, C4 and C5 occupying the equatorial positions. The coordination geometry is distorted from ideal trigonal–bipyramidal (τ parameter 0.77; Addison *et al.*, 1984), with $C_{eq}—Cr—C_{eq}$ bond angles in the range 115.4 (2)–124.0 (3)°, $C_{eq}—Cr—C_{ax}$ bond angles in the range 84.2 (2)–94.8 (2)° and a $C_{ax}—Cr—C_{ax}$ angle of 170.0 (2)°. The O—C—Cr bond angles are nearly linear [175.7 (4)–179.3 (5)°], consistent with the geometry of previously reported $[2,2,2\text{-crypt-K}]_2[Cr_2(CO)_{10}]$ [174.14 (12)–178.80 (12)°]. The axial Cr—C bonds in (I) are longer than the equatorial bonds, although the differences are significant at the 3σ level only for the Cr1—C3 bond. The axial and equatorial C—O bond

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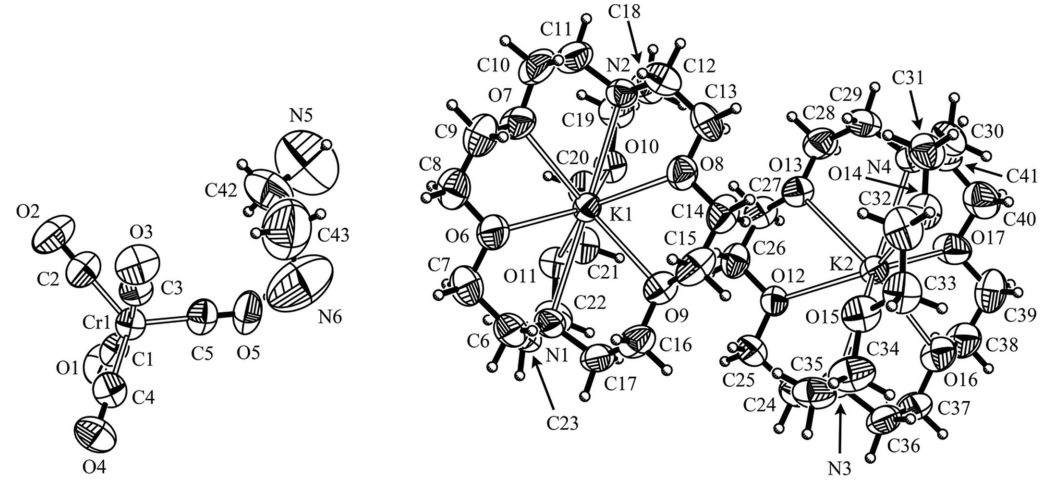

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted.

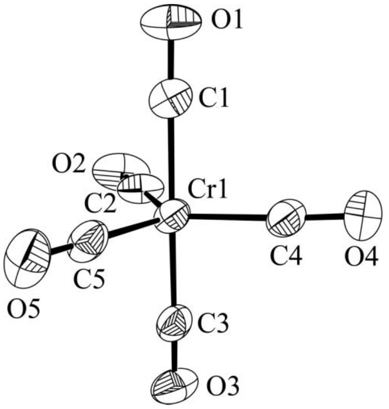

Figure 2
The molecular structure of the $[Cr(CO)_5]^{2-}$ anion in (I), with displacement ellipsoids drawn at the 30% probability level.

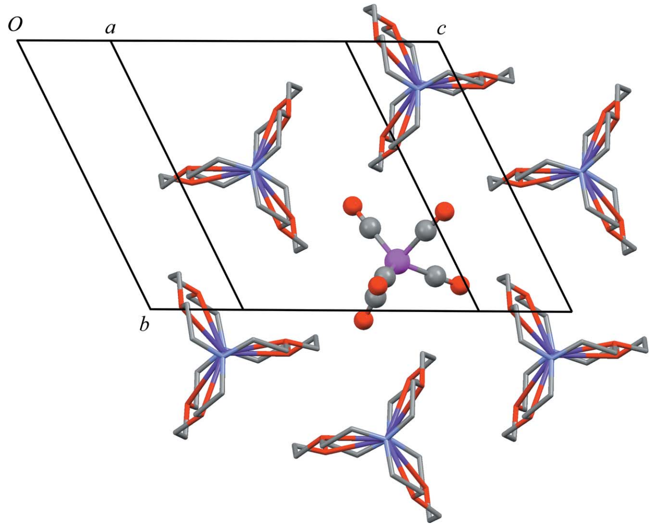

Figure 3
A view of (I), projected onto (100). The hexagonal arrangement of [2,2,2-crypt-K]$^+$ cations is shown, together with one $[Cr(CO)_5]^{2-}$ anion occupying the void within and between the hexagonal layers. The ethylenediamine solvent molecule, also located in the void, has been omitted.

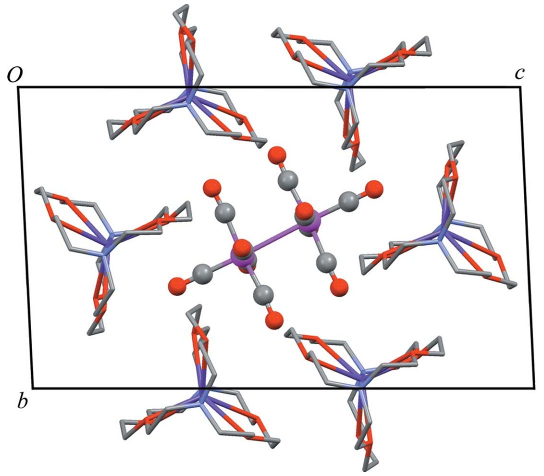

Figure 4
A view of [2,2,2-crypt-K]$_2$[$Cr_2(CO)_{10}$] (Borrmann *et al.*, 1997*b*), showing the hexagonal arrangement of [2,2,2-crypt-K]$^+$ cations and $[Cr_2(CO)_{10}]^{2-}$ anions, comparable with (I).

lengths do not differ significantly at the 3σ level. The average axial Cr—C bond [1.843 (6) Å] is longer than the corresponding average bond in the various reported $[Cr_2(CO)_{10}]^{2-}$ dianions (Table 2), while the average equatorial Cr—C bond [1.821 (6) Å] is shorter. In the structure of [2,2,2-crypt-K]$_2$[$Cr_2(CO)_{10}$] (Borrmann *et al.*, 1997*b*), the axial Cr—C bonds are shorter than the equatorial bonds, and the axial C—O bonds are consequently longer than the equatorial bonds. This is consistent with greater electron back-donation from the metal centres onto the axial carbonyl ligands in that case. In $[Cr(CO)_5]^{2-}$ within (I), the axial Cr—C bonds are longer than the equatorial bonds, indicative of less electron back-donation to the axial carbonyl ligands.

Experimental

The extreme air- and moisture-sensitive nature of the compounds required all manipulations to be carried out under rigorously anhydrous conditions. As a result, all reactions were performed in a drybox under an N_2 atmosphere. $K_3Cd_2Sb_2$ was prepared by direct fusion of a stoichiometric ratio of the elements in Nb containers that were placed into fused silica tubes to protect them from air. The temperature treatment involved heating to 1000 K, holding for a period of 4 d, then cooling slowly (at a rate of 2 K h^{-1}) to room temperature. The 2,2,2-crypt ligand was purchased from Acros and dried carefully under vacuum before use. Ethylenediamine was redistilled from CaH_2 under N_2. Toluene was dried and kept over Na. $K_3Cd_2Sb_2$ (0.105 mmol, 61.5 mg) and 2,2,2-crypt (0.216 mmol, 81 mg) were dissolved in ethylenediamine (2 ml) to yield a dark-red solution. $Cr(CO)_6$ (0.21 mmol, 46.2 mg) dissolved in toluene (1 ml) was added dropwise, and the reaction mixture was left to stand at room temperature for 2 h with occasional stirring. The resulting dark-red solution was filtered and carefully layered with toluene (6 ml). Red crystals of (I) suitable for X-ray analysis were obtained within 3 d. Elemental analysis found: C 47.58, H 7.51, N 7.63%; calculated: C 47.67, H 7.44, N 7.56%.

Crystal data

$[K(C_{18}H_{36}N_2O_6)]_2[Cr(CO)_5]\cdot C_2H_8N_2$
M_r = 1083.33
Triclinic, $P1$
a = 11.034 (3) Å
b = 11.741 (4) Å
c = 12.818 (3) Å
α = 63.883 (7)°
β = 66.841 (10)°
γ = 86.820 (13)°
V = 1356.9 (7) $Å^3$
Z = 1
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 293 K
0.42 × 0.41 × 0.28 mm

Data collection

Rigaku Saturn 70 CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.838, T_{max} = 0.888
10684 measured reflections
7850 independent reflections
5037 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.120
S = 0.96
7850 reflections
623 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.28 e $Å^{-3}$
Absolute structure: Flack (1983), with 578 Friedel pairs
Flack parameter: 0.49 (3)

Table 1
Selected geometric parameters (Å, °).

Cr1—C1	1.841 (5)	O1—C1	1.157 (6)
Cr1—C2	1.824 (5)	O2—C2	1.179 (6)
Cr1—C3	1.844 (5)	O3—C3	1.184 (6)
Cr1—C4	1.819 (5)	O4—C4	1.183 (6)
Cr1—C5	1.818 (5)	O5—C5	1.178 (6)
C1—Cr1—C2	86.4 (2)	C2—Cr1—C4	124.0 (3)
C1—Cr1—C3	170.0 (2)	C2—Cr1—C5	120.5 (2)
C1—Cr1—C4	88.1 (2)	C3—Cr1—C4	94.3 (2)
C1—Cr1—C5	93.0 (2)	C3—Cr1—C5	94.8 (2)
C2—Cr1—C3	84.2 (2)	C4—Cr1—C5	115.4 (2)

The relatively large displacement ellipsoids of the ethylenediamine molecule indicate some degree of disorder (static or dynamic). The highest peaks in the residual electron density are also located close to this molecule, but they are small (0.36 e $Å^{-3}$ or less) and disorder was not modelled explicitly. The H atoms of the NH_2 groups were placed geometrically in staggered positions compared to the neighbouring methylene groups. For both NH_2 groups, one of the three possible staggered positions formed unacceptably short H···H contacts to neighbouring molecules, and the other two positions were therefore retained. In the final refinement, H atoms were refined using a riding model, with C—H = 0.99 Å and N—H = 0.89 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. The crystal was treated as an inversion twin, with explicit refinement of the Flack parameter (Flack, 1983).

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Table 2
Average Cr—C bond lengths (Å) in reported $[Cr_2(CO)_{10}]^{2-}$ anions.

Cation	Axial	Equatorial	Reference
$[2,2,2\text{-crypt-K}]^+$	1.813 (2)	1.881 (6)	Borrmann *et al.* (1997*b*)
$[2,2,2\text{-crypt-Na}]^+$	1.828 (2)	1.876 (4)	Borrmann *et al.* (1997*a*)
K^+	1.802 (6)	1.861 (6)	Hey-Hawkins & von Schnering (1991)
PPN^+	1.792 (4)	1.879 (4)	Lee *et al.* (1996)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3018). Services for accessing these data are described at the back of the journal.

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